# Desulfurization Sorbents for Transport-Bed Applications

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## Introduction

Advanced power generation systems employing gasification of carbonaceous fuels offer increased efficiency and reduced emissions over pulverized coal-fired boiler systems currently in service. Integrated gasification combined cycle (IGCC) is the leading gasification-based system which is being advanced worldwide to produce electricity from carbonaceous fuels. This technology has the potential to reduce sulfur and nitrogen emissions—the precursors of "acid-rain"—and could lead to significant reductions in carbon dioxide emissions, which, it is believed, are major contributors to global warming. Successful commercialization of the IGCC technology requires economic competitiveness with other power generation systems. This economic competitiveness has propelled research and development of gas desulfurization systems.

A number of mixed metal oxide sorbents have been investigated for removal of reduced sulfur species ($H_2S$, COS, $CS_2$, etc.) at high-temperature, high-pressure (HTHP) conditions (Gupta and Gangwal, 1992); the best candidates have been the ZnO-based sorbents because of their ability to reduce the fuel gas sulfur level to a few parts per million by volume (ppmv). The work described in this paper deals with the development of zinc titanate sorbents for transport reactor applications.

Early designs and previous research work involving gas desulfurization sorbents were based on fixed-bed reactors because of their simplicity of operation (Gangwal, 1991). However, recent research has concentrated on fluidized-bed systems because of the potential of such systems to be made continuous in operation and to handle the temperature rise due to the high exothermicity of the regeneration reaction (Gupta and Gangwal, 1992). Conventional (bubbling-type) fluidized-bed reactors have been successfully used on a semicommercial scale for gas desulfurization by Ishikawajimi-Harima Heavy Industries (IHI) in Japan and Enviropower in Finland. The M.W. Kellogg Company has adapted the transport reactor technology, which was originally developed for fluid catalytic cracking (FCC) applications, for gas desulfurization. As outlined in Henningsen et al. (1997), the transport reactors have significant advantages over conventional fluidized-bed reactors including:

- The required sorbent inventory is much smaller, as gas velocities are about 20 to 40 times higher and riser gas-to-solid volume ratios are much smaller.

- The time of sorbent exposure to a reactive gas environment is on the order of 1 to 2 seconds during both absorption and regeneration.

- A transport reactor can handle a feed gas containing fines (not captured by the cyclone), thus eliminating the need for an upstream barrier filter.

- Only a slipstream of circulating solids is used for regeneration; hence, control of temperature rise is easier and no diluent is required to absorb the heat.

- The amount of sulfur absorbed and regenerated per cycle is between 2 and 4 wt%, thus eliminating the need for a high sulfur capacity sorbent.

With the adaptation of transport reactor technology to gas desulfurization by M.W. Kellogg in the Piñon-Pine Clean Coal Technology demonstration project, an immediate need for sorbents for transport reactor application was recognized. In the Piñon-Pine plant, a majority of the sulfur removal takes place within the gasifier with limestone/dolomite sorbents. An external gas desulfurization system based on the transport reactor technology is used as a polishing bed to reduce the sulfur level of coal gas below 20 ppmv. For transport reactor applications, a sorbent must

- Possess and maintain high chemical reactivity for removing sulfur species from coal gas within 1 to 2 seconds of residence time.

- Maintain an attrition rate below design specifications.

- Be regenerable with neat air to maintain cyclic operation.

- Possess good flow characteristics.

- Be competitively priced.

Initial efforts to produce suitable sorbents for this application by spray drying led to development of the CMP-107 sorbent (Gupta et al., 1998). The CMP-107 sorbent was manufactured by Contract Materials Processing (CMP), Inc., of Baltimore, Maryland. Pilot-scale testing of this sorbent at M.W. Kellogg indicated that the sorbent readily removed $H_2S$ to <5 ppmv (the analytical detection limit), but its attrition rate was more than twice the target value that M.W. Kellogg used in the transport reactor design for the Piñon-Pine plant (Gupta et al., 1996a).

## Objectives

This project extends the prior work on the development of fluidizable zinc titanate particles using a spray-drying technique to impart high reactivity and attrition resistance. The specific objectives are:

- To develop highly reactive and attrition-resistant zinc titanate sorbents in 40- to 150-$\mu$m particle size range for transport reactor applications

- To provide technical support to Sierra Pacific Power Company (SPPCo) for their Piñon-Pine Clean Coal Technology Demonstration plant.

## Approach

Comprehensive analysis of results obtained during bench-scale testing at the Research Triangle Institute (RTI), transport reactor test unit (TRTU) testing at M.W. Kellogg, and modular gas cleanup rig (MGCR) testing at the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) as reported in Gupta et al. (1996b) with the CMP-107 sorbent indicated that a proper combination of reactivity and attrition properties is necessary to minimize the impact of sorbent costs on operation of the gas desulfurization unit in an IGCC plant. Figure 1 depicts the interrelationship of various process parameters involved in the sorbent selection process. All the sorbent properties (as shown in Figure 1) must be considered for selecting a suitable sorbent for transport reactor applications. For example, a sorbent with very high reactivity and poor attrition resistance may not be cost-effective, as it will require frequent replenishment. Alternatively, a sorbent with very high attrition resistance and poor reactivity may not be suitable, as it will not remove the desired amount of sulfur species in the specified residence time. Therefore, research efforts were focused on improving the attrition resistance of spray-dried zinc titanate sorbents while maintaining their chemical reactivity, sulfur capacity, and regenerability.

## Project Description

This project is a collaborative effort with Intercat Development, Inc., of Sea Girt, New Jersey, a commercial catalyst manufacturer specializing in spray-drying FCC additives for petroleum

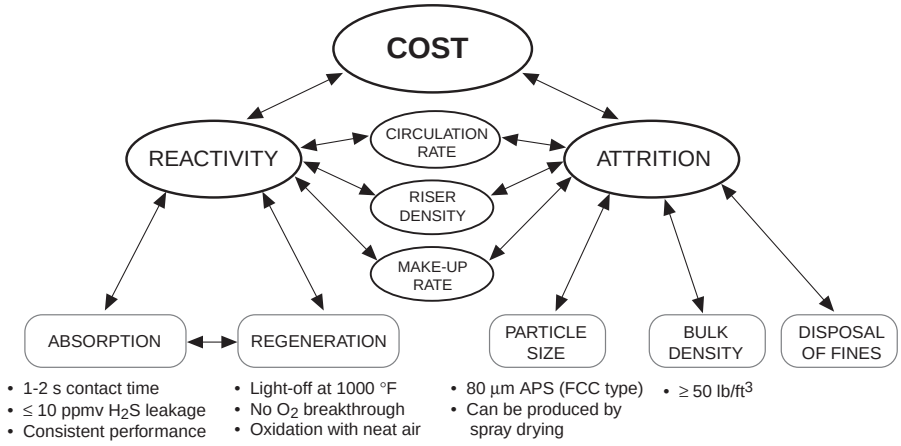


**Figure 1. Criteria for commercial sorbent selection.**

refineries and the M.W. Kellogg Company of Houston, Texas, that developed the transport reactor technology for hot-gas desulfurization. Intercat also had a grant (No. DE-FG02-96ER82189) under Small Business Innovation Research (SBIR) Phase II from DOE. RTI and Intercat entered into a teaming agreement to jointly develop and commercialize the spray-dried zinc titanate sorbents.

Target density, attrition resistance, and particle characteristics for zinc titanate sorbents were very similar to properties of products developed by Intercat for use in FCC processes. The primary goal was to maximize zinc titanate sorbent activity while maintaining maximum attrition resistance.

As discussed in Gupta et al. (1997), Intercat has developed and patented several binder technologies for manufacturing of attrition-resistant microspheres for use in FCC petroleum refining processes. These technologies have been adapted to several Intercat products for use in FCC processes. Examples include sorbents for regenerator $SO_x$ adsorption, zeolites, and metal trapping materials for catalytic cracking.

Using their patented binder technologies, Intercat prepared a number of zinc titanate sorbent compositions. As described in Gupta et al. (1997), screening and characterization of these sorbent formulations led to the development of the EX-S03 formulation. A number of HTHP tests were performed in RTI's bench-scale sorbent test facility to demonstrate chemical reactivity and regenerability of the sorbent. A 1,000-pound batch of this material was produced in a commercial-scale spray dryer to demonstrate the scaleup of the manufacturing process. Details of the composition and the manufacturing process for the EX-S03 sorbent are proprietary to Intercat and RTI.

The HTHP bench-scale sorbent test facility at RTI (shown in Figure 2) can operate at up to 400 psi pressure and 1,600 °F temperature and can handle corrosive gases such as HCl, $H_2S$, and $SO_2$ in the presence of steam. The gas delivery system for this unit consists of eight electronic mass flow controllers (MFCs)and one high-pressure liquid chromatography (HPLC) pump. A 2-in. ID quartz reactor is housed in a 4-in. ID stainless steel pressure vessel. The gas analysis system consists of two online gas chromatographs (Varian 3300 with a flame photometric detector [FPD] for sulfur gases and Hewlett Packard 5890 with a thermal conductivity detector [TCD] for permanent gases), two continuous $SO_2$ analyzers, an oxygen analyzer and a $CO_2$ analyzer. Real time data acquisition and process control are accomplished by an advanced hardware/software package obtained from National Instruments.

Two multicycle HTHP tests were carried out at RTI with the EX-S03 sorbent (from the 1,000-pound batch) to determine its long-term chemical reactivity and mechanical strength. Each test consisted of 10 sulfidation-regeneration cycles. The first test simulated conditions in Kellogg's TRTU, while the second test was performed to mimic operating conditions expected at the Piñon-Pine plant.

Pertinent findings of these HTHP tests indicated that sorbent was capable of reducing the $H_2S$ concentration of simulated coal gas from 2,000 to 20 ppmv at 1,000 °F. Regeneration of this

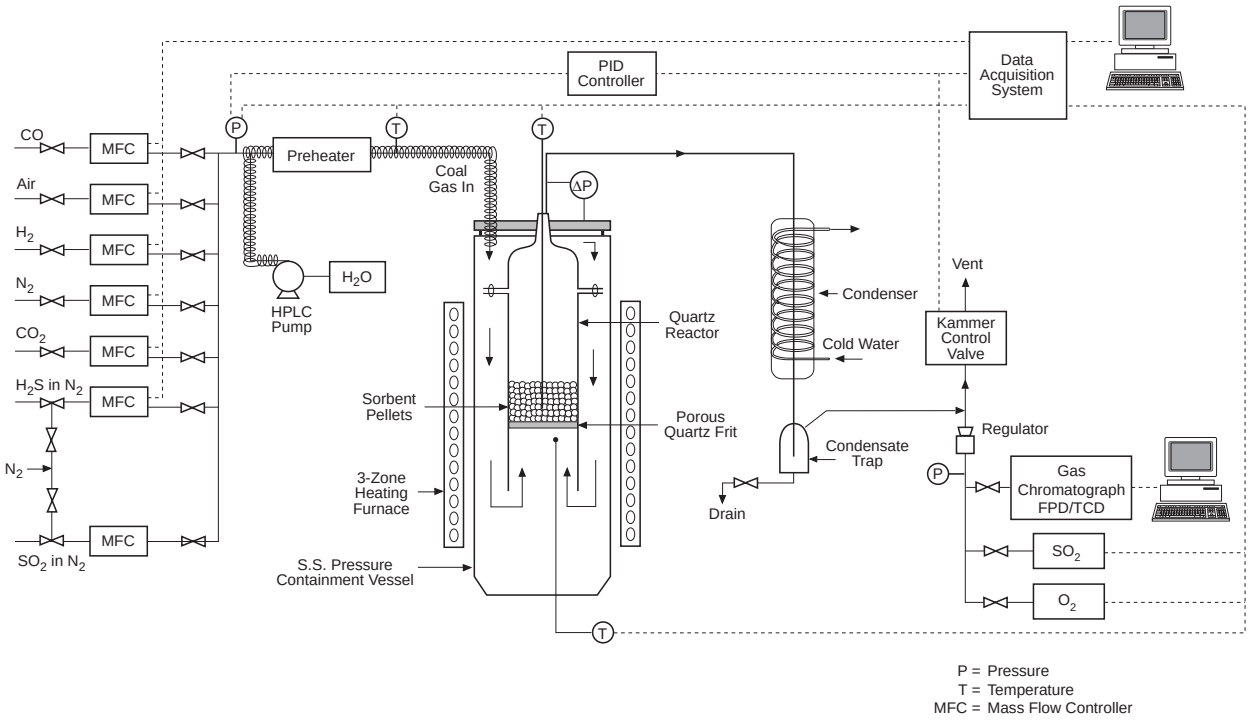


**Figure 2. RTI bench-scale test facility.**

sorbent required an initial temperature of about 1,150 °F. However, as indicated previously, the sorbent must initiate regeneration at 1,000 °F or below to be suitable for use at Piñon-Pine. To alleviate this problem, RTI developed a lightoff additive, which, when added in small quantities to the sorbent, was capable of initiating the regeneration in an 800 to 1,000 °F range. During these HTHP tests, regeneration of the EX-S03 sorbent was successfully demonstrated at an initial temperature of 1,000 °F with stoichiometric $SO_2$ formation. Posttest characterization of the reacted sorbent (after the 10th regeneration) showed improvement in chemical reactivity and attrition resistance over the fresh sorbent (Gupta et al., 1997).

Following successful HTHP bench testing at RTI, TRTU testing of EX-S03 zinc titanate was carried out at Kellogg to determine its suitability for use at the Piñon-Pine plant. Two batches of sorbent from the same lot were tested in the TRTU. The first batch was subjected to three sulfidations and two regenerations and then circulated in the Cold Flow Model to study its flow properties and to determine its attrition. The second batch was tested over eight cycles of $H_2S$ absorption and regeneration of the sulfided sorbent in order to determine the change in sulfur absorption capacity with the number of cycles and attrition characteristics.

Pertinent findings of the TRTU test done at Kellogg are listed below.

- Absorption of $H_2S$ was very good with essentially no leakage of $H_2S$ (<20 ppmv) in the outlet gas when sorbent was not near saturation and when the inlet $H_2S$ concentration was below 6,000 ppm.

- The sorbent underwent conditioning as observed by the improvement in performance after the first cycle.

- The sulfur absorption capacity of the fresh sorbent was about 9 wt% at $H_2S$ breakthrough (at 1,000 ppm in the exit gas). The sulfur absorption capacity did not change with cycles. There was no loss in sulfur absorption capacity after eight cycles. These sorbent capacity values were confirmed by chemical analysis of sorbent for sulfide sulfur.

- A temperature of 1,000 to 1,200 °F was required to regenerate the sorbent.

- The regeneration of sorbent over eight cycles was good; there was no $O_2$ breakthrough and expected peak $SO_2$ concentration indicated that no sulfate was formed during regeneration. This was confirmed by the chemical analysis of the sorbent.

- The sorbent attrition rate estimated based on the size distributions of the feed, the bed drain, and the amount of filter fines collected at the end of eight cycles in the test indicated that the amount of fines generated was about $7.5 \times 10^{-6}$ lb/lb of sorbent circulated based on the amount of fines below 22 µm. This value was an order of magnitude smaller compared to any sorbent previously tested in the TRTU. For CMP-107 sorbent jointly developed by RTI/CMP, this value was $5 \times 10^{-5}$ lb/lb of sorbent circulated based on amount of fines below 11 µm. This attrition rate amounts to about 4.5 lb/h loss of sorbent at Piñon-Pine desulfurizer based on the solid circulation rate. This is much less than expected and represented a significant performance improvement compared to any previously tested sorbents.

## Results

### Sorbent Production and Qualification Testing for the SPPCo

Based on the bench-scale and TRTU testing results, SPPCo ordered a batch of the EX-S03 sorbent from Intercat. This sorbent batch was loaded into the external desulfurizer at Piñon-Pine and was successfully circulated without attrition problems. Currently, the sorbent is loaded in the desulfurizer and is awaiting full evaluation (including sulfur removal efficiency, regenerability, and attrition under reaction conditions) with the startup of the Piñon-Pine IGCC plant.

Prior to shipping the sorbent batch to SPPCo, extensive bench-scale testing was conducted to ensure that sorbent met the specifications provided by SPPCo. From their prior experience with other sorbent materials, SPPCo was quite concerned about the attrition resistance of the sorbent. While ordering the sorbent batch, SPPCo specified that the attrition index (AI) (as measured by Intercat) should be below 5 and preferably below 2 to minimize sorbent loss from the desulfurizer due to mechanical attrition. Table 1 compares AI values of the commercial material supplied to SPPCo to the previous generation materials developed by RTI, RTI-CMP, and RTI-

**Table 1. Attrition Index for Various Generations of Zinc Titanate Sorbents**

| Material | Description | Attrition index |
|---|---|---|
| ZT-4 | Granulated zinc titanate sorbent | >25 |
| CMP-107 | Earlier spray-dried zinc titanate sorbent developed by RTI-CMP | >25 |
| FCC | Commercial fluid-catalytic cracking catalyst | <5 |
| EX-S03 | Earlier version of zinc titanate material developed by Intercat-RTI and used in bench-scale and pilot-plant testing | 4.0 |
| EX-S03 | Commercial material supplied to SPPCo | 1.4 |

Intercat. Also included in table is the AI of a commercial FCC catalyst for comparison purpose. The AI of the sorbent batch supplied to SPPCo was 1.4 compared to 4.0 for the previous generation material. This value of the AI was independently confirmed by M.W. Kellogg.

Besides attrition, the sorbent was tested for its chemical reactivity and regenerability. A series of tests were conducted in RTI's HTHP bench-scale test facility under test conditions simulating the temperature, pressure, gas composition, and residence time in the desulfurizer at Piñon-Pine. Figure 3 shows a typical breakthrough curve plotted as $H_2S$ concentration as a function of sulfur loading for this sorbent. As can be seen, the sorbent met the $H_2S$ leak as well as sulfur loading targets.

As discussed previously, in order for the EX-S03 sorbent to initiate regeneration under neat air conditions at 1,000 °F or below, a lightoff additive was needed. In parallel to the sorbent development work at RTI and Intercat, efforts continued to develop a lightoff additive for this application. RTI researchers discovered a composition suitable for this application. After initial feasibility tests with the composition, Intercat and RTI jointly worked and developed this additive as a commercial material. Intercat produced a batch of this material, designated as LOA-1, for the Piñon-Pine plant.

Figure 4 shows regeneration temperature profiles for the EX-S03 material mixed with the LOA-1 additive. This regeneration test was conducted with neat air in a bubbling fluidized bed. As can be seen, sorbent regeneration was initiated at 800 °F. The maximum temperature achieved was about 1,400 °F. These data clearly indicate that with the LOA-1 sorbent should easily regenerate at 1,000 °F with neat air.

Figure 5 shows the $SO_2$ and $O_2$ evolution profiles for the above regeneration. As seen, the peak concentration of $SO_2$ is 14 vol%, which will correspond to 21 vol% $O_2$ in neat air, thus indicating no sulfation problems. A number of additional tests confirmed no deleterious effect of system upsets at Piñon-Pine on the sorbent performance.

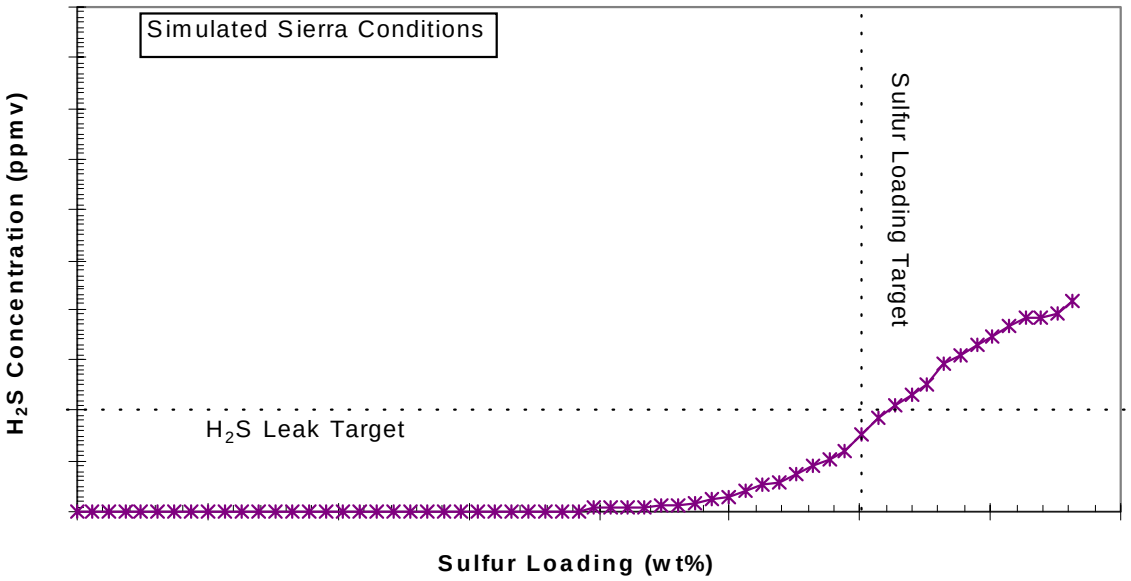


**Figure 3. A typical breakthrough curve for the commercial material supplied to SPPCo.**

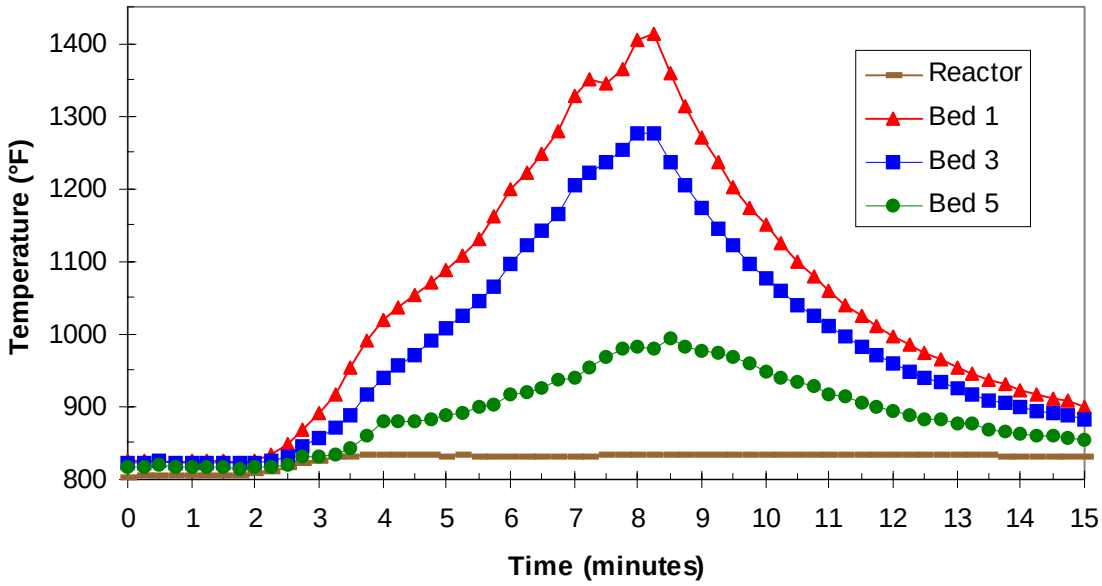


**Figure 4. Regeneration temperature profiles for the commercial material mixed with the LOA in RTI's HTHP bench unit.**

## Sorbent Testing with "Real" Coal Gas

In addition to bench-scale testing of the commercial material at RTI, this sorbent was also tested at DOE/FETC facilities in Morgantown, West Virginia, with "real" coal gas generated in a

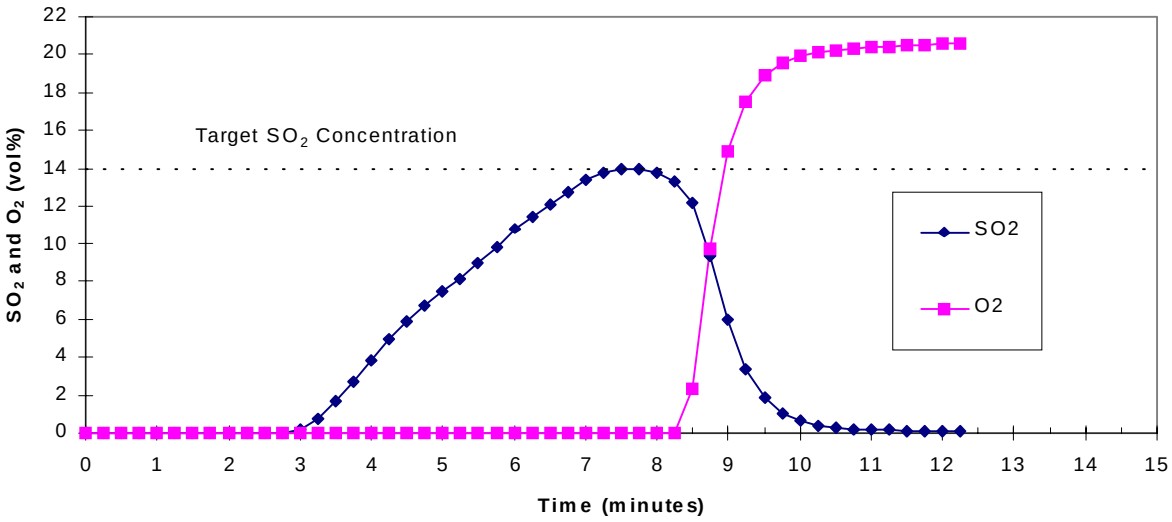


**Figure 5. $SO_2$ and $O_2$ evolution profiles during regeneration of the commercial material in RTI's HTHP bench-unit.**

fluidized-bed gasifier. Two sets of tests were conducted. The first set was done in the MGCR which is a bubbling fluidized-bed reactor capable of operating at HTHP conditions with "real" coal gas. Essentially, it is a scaled-up version of the RTI's unit operating with "real" coal gas. Fourteen sulfidation-regeneration cycles were performed in the MGCR. The second test was conducted in the transport reactor facility (TRF) which, to some extent, simulates the riser at Piñon-Pine. In addition to testing the sorbent in larger units, the main objective of these tests was to determine any deleterious effect of heavy metals and chloride present in real coal gas on the sorbent performance.

Figure 6 shows a typical sulfidation behavior of the EX-S03 sorbent at 280 psig and 1,000 °F in the MGCR. It is to be noted that the inlet $H_2S$ concentration varied significantly over the test duration. The outlet $H_2S$ concentration throughout the sulfidation was below the detection limit of the measurement instrument (<100 ppmv). These results clearly indicate that the sorbent is capable of reducing $H_2S$ levels to very low levels without being affected by any other coal gas contaminants such as heavy metals and chlorides.

Figure 7 shows a typical regeneration behavior in the MGCR. Both temperature and $SO_2/O_2$ evolution data are included in this figure. This regeneration was done with 7 vol% $O_2$ in $N_2$. No attempts were made to regenerate the sorbent with neat air because of safety concerns arising from excessive temperature rise. The TI-300 thermocouple was about 2-in. below the gas distributor and indicates the temperature of the regeneration inlet gas. The furnace settings to the MGCR were about 1,050 °F to obtain a sorbent bed temperature of about 1,000 °F. The thermocouples TI-301, TI-302, TI-303, and TI-304 were inside the sorbent bed at locations 2, 6, 10, and 18-in. above the distributor plate, respectively. The peak temperature observed during these regenerations was between 1,400 and 1,500 °F. The peak $SO_2$ concentration was about 5.5 vol%. These regenerations confirmed stoichiometric $SO_2$ formation, without any sulfation problems.

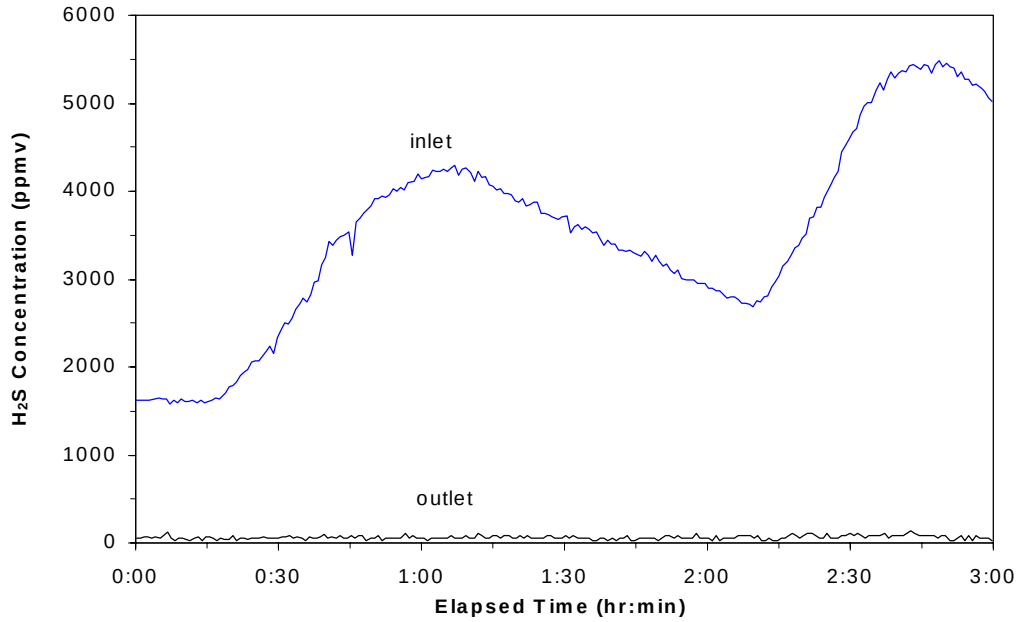


**Figure 6. Sulfidation behavior of the commercial material in DOE/FETC's MGCR.**

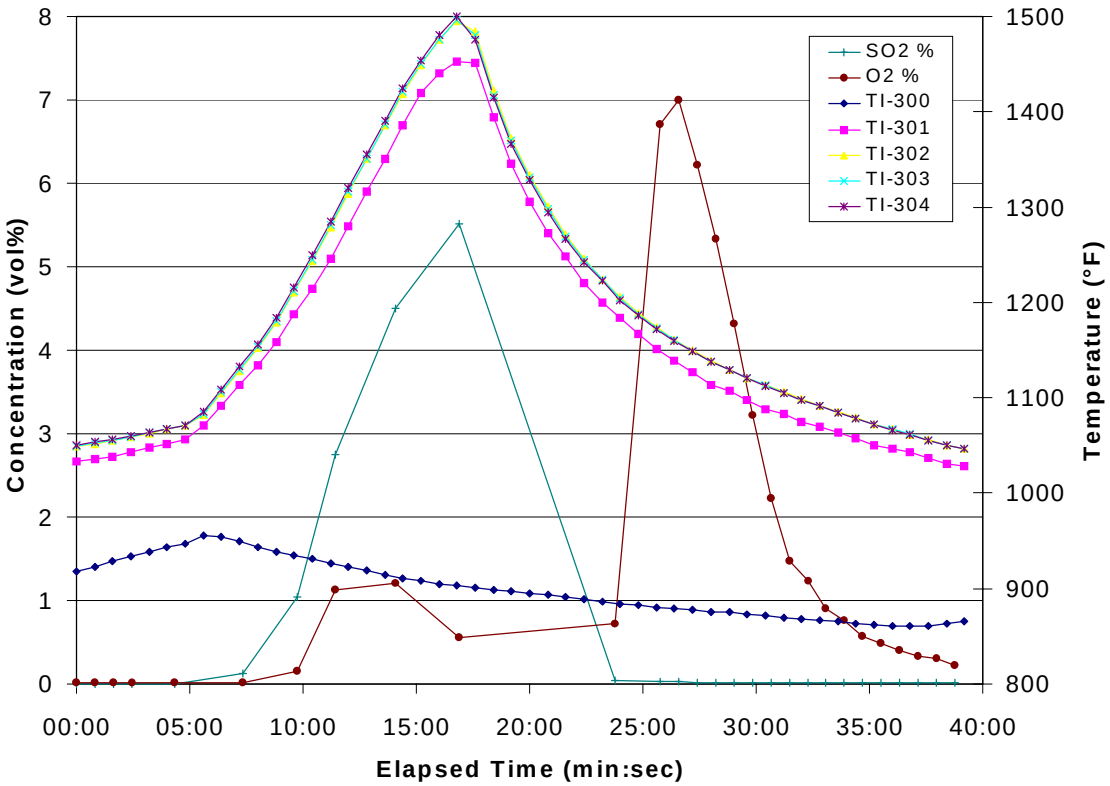


**Figure 7. Regeneration behavior of the commercial material in DOE/FETC's MGCR.**

After the 14 cycles of testing, the sorbent was removed and characterized for its physical and chemical properties. Figure 8 shows a comparison of TGA reactivities of the fresh and reacted material. An improvement in the chemical reactivity is seen, as would be expected, based on previous bench-scale results obtained at RTI (Gupta et al., 1997). The attrition resistance of the reacted material also improved and changes in other properties were small. Analysis of reacted material for heavy metals and chloride indicated essentially no sequestering of these compounds.

Testing of this material was also conducted in the TRF with real coal gas conditions. The average particle size (APS) and sulfur loading were measured after each pass in the TRF. Figure 9 shows the weight percent sulfur as a function of pass number for two independent tests (Intercat A and Intercat B). These results indicate that sorbent continued to capture sulfur with time. Figure 10 shows APS as a function of pass number for two independent sets. No significant change in particle size is seen with time, indicating minimal attrition of the sorbent.

## Conclusions

A highly attrition-resistant and chemically reactive zinc titanate sorbent was developed for transport reactor applications. This development effort not only identified an optimal material formulation, but also established and demonstrated commercial production procedures. Commercial grade samples of this sorbent have been extensively tested in both bubbling-bed and transport pilot-scale reactors. The sorbent's performance at DOE/FETC facilities with real coal

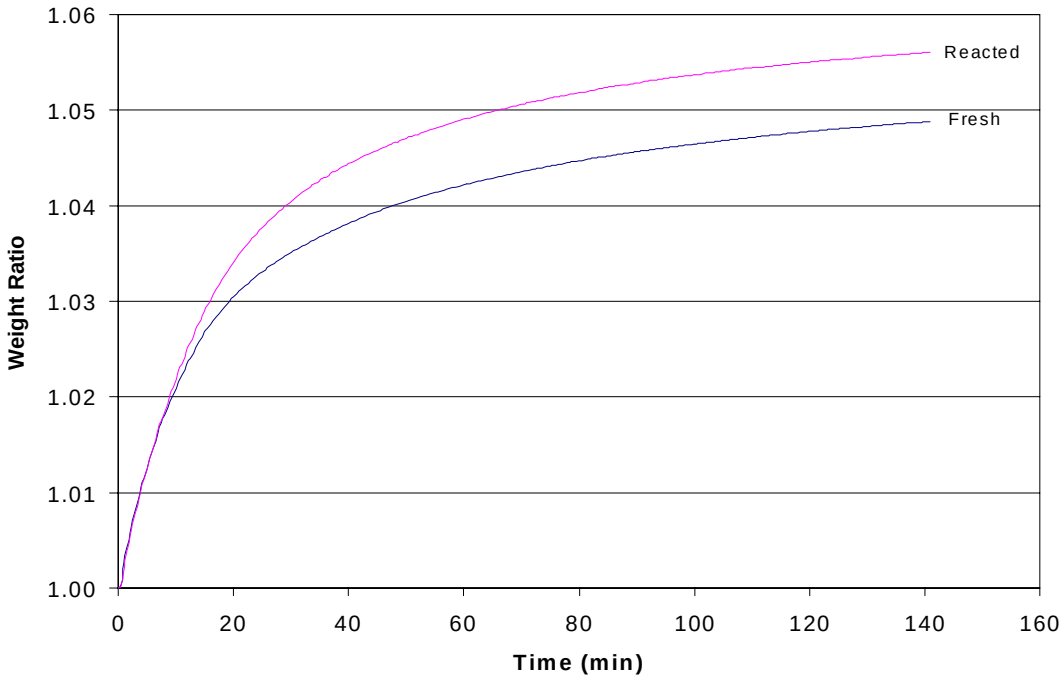


**Figure 8. TGA reactivities of fresh and reacted (removed after MGCR testing) zinc titanate sorbent.**

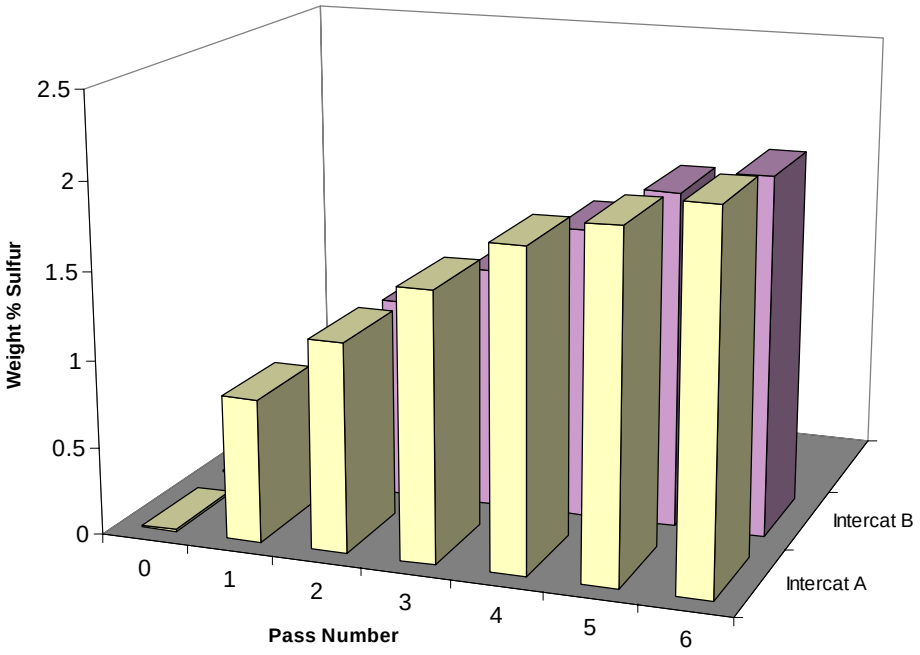


**Figure 9. Sulfur loading of the commercial material in DOE/FETC's TRF.**

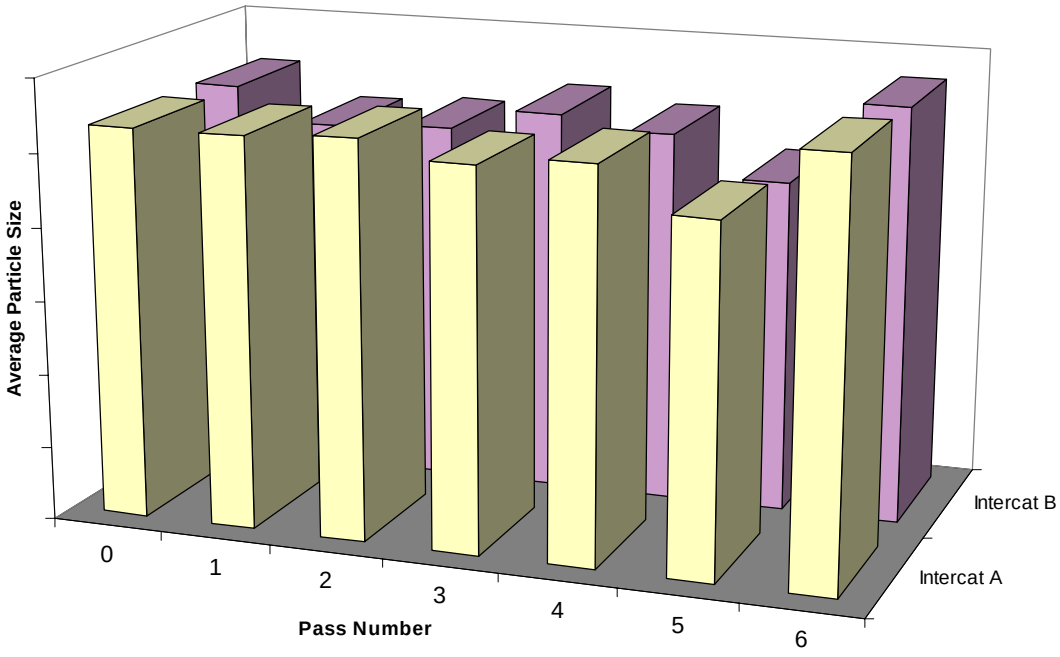


**Figure 10. Average particle size of the commercial material as a function of pass number in DOE/FETC's TRF.**

gas was consistent with the performance observed in previous testing. The trace contaminants present in real coal gas, particularly the heavy metals and chlorides, did not affect sorbent performance and were not sequestered on the sorbent. Sufficient commercial grade sorbent was provided to SPPCo to fill the external desulfurization unit at the Piñon-Pine plant. The sorbent has been successfully circulated without attrition problems and is awaiting full evaluation. In conjunction with the sorbent development, a regeneration lightoff additive was developed to facilitate the initiation of sorbent regeneration at $\leq$1,000 °F. Development and testing of this additive were sufficiently advanced to permit supplying SPPCo a commercial batch of this light-off additive with the sorbent.

## Applications

The success of IGCC technology is greatly dependent on the development of cost-effective processes for the removal of contaminants, particularly sulfur, from syngas. Currently, a sorbent prepared by Intercat and RTI awaits commercial testing in the external desulfurizer at SPPCo's Piñon-Pine plant. Based on extensive testing of this sorbent, the chemical and physical properties of this sorbent met, if not exceeded, the requirements established for the external desulfurizer.

The long-term beneficiary of IGCC technology will be chemical plants nationwide and world-wide as an economical alternative clean fuel source becomes available for both energy and chemical production. The ability to utilize a variety of carbonaceous feedstocks with only minor modifications makes this technology very versatile. One important area of application is the gasification of carbonaceous waste materials typically found at petroleum refineries. As these wastes contain between 3 and 10 wt% sulfur, generating a clean fuel gas for either power production via combustion in a gas turbine or chemical synthesis requires a reliable process for sulfur removal. Successful commercial demonstration of the external desulfurizer at Piñon Pine would establish the reliability of this process.

## Future Activities

Sorbent development work will have two components after successful commercial demonstration of the desulfurization technology. The first will involve improving the sorbent by increasing the amount of sulfur removed, lowering the amount of sulfur remaining (i.e., to sub-ppmv levels) in the gas after treatment, increasing the rate at which sulfur is absorbed and achieving similar improvements for sorbent regeneration. Alternatively, sorbent development will focus on modifying the sorbent's properties for specialized niche applications of the desulfurization technology.

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## References

Gangwal, S.K. 1991. "Hot-Gas Desulfurization Development for IGCC." In *IChemE Symposium Series*. No. 123. Sheffield, UK. pp. 159-170.

Gupta, R., and S.K. Gangwal. 1992. "Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications—Development and Testing of Zinc Titanate Sorbents." Topical Report to DOE/METC. Report No. DOE/MC/25006-3271. Morgantown Energy Technology Center, U.S. Department of Energy, Morgantown, WV. NTIS/DE93000247. November.

Gupta, R., S.K. Gangwal, D.C. Cicero, G.B. Henningsen, and S. Katta. 1996a. "Hot Coal Gas Desulfurization in Fluidized-Bed Reactors Using Zinc Titanate Sorbents." In *High Temperature Gas Cleaning*, published by Institut für Mechanische Verfahrenstechnik und Mechanik der Universität Karlsruhe (TH), Karlsruhe, Germany, September, pp. 543-556.

Gupta, R., et al. 1996b. "Bench-Scale Development of Fluidized-Bed Spray-Dried Sorbents." Paper #96PS3-4. In *Proceedings of Advanced Coal Fired Power Systems Meeting*, Morgantown, WV. July 16-18.

Gupta, R., B.S. Turk, and A.A. Vierheilig. 1997. "Desulfurization Sorbents for Transport-Bed Applications. In *Proceedings of The Advanced Coal-Based Power and Environmental Systems '97 Conference*, Pittsburgh, PA, Paper 2A-6, July. Report No. DOE/FETC-97/1046 (NTIS/DE97005454).

Gupta, R., S.K. Gangwal, and S.C. Jain. 1998. "Zinc Titanate Sorbents." U.S. Patent No. 5,714,431, February 3.

Henningsen, G.B., S. Katta, and G.K. Mathur. 1997. Sorbent Testing and Commercialization of Transport Reactors for Hot-Gas Desulfurization." In *Proceedings of The Advanced Coal-Based Power and Environmental Systems '97 Conference*. Pittsburgh, PA, Paper 2A-7, July. Report No. DOE/FETC-97/1046 (NTIS/DE97005454).